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Electrospinning of polymethyl methacrylate nanofibers: optimization of processing parameters using the Taguchi design of experiments

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Abstract

The effects of polymer concentration and electrospinning parameters on the diameter of electrospun polymethyl methacrylate (PMMA) fibers were experimentally investigated. It was also studied how the controlled factors would affect the output with the intention of finding the optimal electrospinning settings in order to obtain the smallest PMMA fiber diameter. Subsequently the solution feed rate, needle gauge diameter, supply voltage, polymer concentration and tip-to-collector distance were considered as the control factors. To achieve these aims, Taguchi's mixed-level parameter design (L_{18}) was employed for the experimental design. Optimal electrospinning conditions were determined using the signal-to-noise (S/N) ratio that was calculated from the electrospun PMMA fiber diameter according to "the-smaller-the-better" approach. Accordingly, the smallest fiber diameter observed was 228 ($\pm$76) nm and it was yielded at 15 wt% polymer concentration, 20 kV of supply voltage, 1 ml/h feed rate, 15 cm tip-to-distance and 19 needle gauge. Moreover, the S/N ratio response showed that the polymer concentration was the most effective parameter on determination of fiber diameter followed by feed rate, tip-to distance, needle gauge and voltage, respectively. The Taguchi design of experiments method has been found to be an effective approach to statistically optimize the critical parameters used in electrospinning so as to effectively tailor the resulting electrospun fiber diameters and morphology.

Keywords

electrospinning parameters, fiber diameter, polymethyl methacrylate, Taguchi method (design of experiments), optimization

Introduction

The electrospinning process provided the opportunity to fabricate micrometer and nanometer size diameters of polymeric and inorganic fibers.[1,2] The first step of the electrospinning process is carried out by putting a polymer solution into a syringe supplied through a needle connected to a high-power source. The high voltage difference between the needle and the collector, generally in the range of 5–30 kV, can be produced by a high-power source. In the second step of the process, the solvent induces evaporation by electrical charges after the polymer solution is ejected from the syringe. As a result, an elongated polymer fiber will deposit on the collector. In the past, a number of factors were investigated in order to comprehend as well as manage the electrospinning method.[1,3,4]

There are number of scholars who were interested in the fiber diameters and morphology and, indeed, they made several evaluations. However, one prominent phenomenon can be seen when browsing through these articles concerning the influence of parameters on the properties of fibers is the manifestation of the

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vast amount of contradicting observations and also the possible occurrences that these parameters are not affecting in the same manner for all types of polymers and solvents.[1,3,5] Furthermore, it is shown that there is a considerable amount of electrospinning process outputs that is dependable on the adjustment of its parameters. For that reason, this work is conducted to fulfill this requirement as further investigations addressing possible cross-talk between different processing parameters and modifications coming from changes in the spinning configurations are definitely needed.[6,7]

An appropriate static model can be utilized for the electrospinning process to evaluate the effects of the parameters on the fiber diameter. This model is capable of displaying the highest effective factors on the fiber diameters. For this reason, in the empirical studies these parameters are the ones to be focused on. The experimental time could be effectively reduced by a theoretical prediction and a route to comprehend the factors influencing the fiber diameter and morphology.[8,9] For instance, controlling the diameter of the fibers is still a methodological bottleneck. The experimental results show that the lowest fiber diameter can be achieved by the lowest flow rates, while, conversely, the fabrication rate and solution concentration affect the fiber diameter.[5,10] Fortunately, using an appropriate predictive method would supply a route to perform many various options rapidly, without having the cost or time problems of a trial-and-error experiment. Recent research has not yet holistically investigated the optimization of the electrospinning process in a systematic manner. It is conventionally limited to the determination of the physical, thermal and structural properties of electrospun nanofibers/nanocomposites with the fixed processing and material parameters.[1,3,4,11]

The design of experiments (DoE) is a very robust experimental design system technique that can explore the significant factorial effects and optimum conditions in the modern manufacturing industry setting.[12,13] Orthogonal arrays are utilized in the Taguchi method to organize the factors that influence the process and the levels where they should vary. Alternatively, the Taguchi method checks a pair of combinations rather than having to examine every possible combination, such as the full factorial method. In this method, the parameters that influence product quality could be indicated with a minimal number of trials.[14] The Taguchi method is giving the opportunity to be able to evaluate all parameters together or independently. The purpose of this paper is to optimize fiber diameter and understand what are the individual effects of parameters that are solely achievable through this method, not only for the electrospinning process but also for many other production processes.[8,15–17]

Several researchers have focused on the fabrication of polymethyl methacrylate (PMMA) via electrospinning; different achievements have been reported from previous works in terms of fiber diameter, PMMA fiber properties and the effect of individual parameters on the fiber properties.[18–21] In fact, none of them have focused on the individual effects and interaction of the electrospinning parameters on the prediction of fiber diameter. Also, a large fiber diameter and a large number of beads are found to be the main problems with their results.[18] In order to fully recognize the potential of electrospun fibers, it is significant to produce different fiber diameters, which will definitely have an important influence on the performance. For example, filtration and composite materials have potential applications of small fibers.[3,4] It should be noted that other applications, such as drug delivery and catalyst support, have attracted interest due to their high surface area as well as electrospinning of tissue engineering, which is being developed.[1,3,4]

This paper aims to study the effect of polymer concentration and electrospinning parameters on PMMA nanofiber morphology so as to find the optimized condition that yields the finest fibers. In order to do so, a robust statistical Taguchi DoE has been employed. In general, we considered the following questions for careful deliberations: What are the factors instigating these contradicting research findings found predominantly in the PMMA nanofiber production? And also, is there any possibility to have all-inclusive laws of dependencies concerning parameters and fiber morphology?

Materials and methods

Materials

In this work, analytically pure PMMA ($-CH_2C-(CH_3))CO_2CH_3-)_n$, $M_w = 120{,}000$) from Aldrich and N,N-dimethylformamide (DMF), which was received from Labchem Sdn Bhd Co., Malaysia, were utilized for the working fluid. Correspondingly, polymer solution samples were obtained through dissolving 15, 20 and 25 wt% PMMA in a DMF solvent.

Experimental procedures

A precursor solution was prepared using DMF as the PMMA solvent. The typical process was carried out by dissolving an adjusted quantity of PMMA in DMF through vigorous stirring for 24 hours. After stirring, different weight ratios of PMMA solutions were achieved. Subsequently, a 5 ml plastic syringe with different needle gauges, 19, 23 and 27, were utilized to place each polymer solution, attributable to the significance of orifice size in the initiation of the jet.[6,20]

ES30P-30 W/SDPM (Gamma High Voltage Research, Ormond Beach, FL) was used as the source for the high voltage power supply. An appropriate Taylor cone was created for experimentation by using two different voltages – 15 and 20 kV – in which the high voltage was connected to a needle through an alligator clip. Then, a ground target covered with aluminum foil was used as the counter electrode, at three different tip-to-distances of 10, 15 and 20 cm. In addition, a syringe pump (NE-300, New Era Pump Systems, Inc.) was used in order to control the feed rate at three different rates: 1, 2 and 4 ml/h.

In view of the fact that the choice of the temperature and relative humidity (RH) are important,[19] the electrospinning process was performed at 25°C and 32% RH. Modification of the polymer concentration, needle gauge, the collection distance and the feed rate was executed to obtain controllable nano-fiber polymer materials.

The morphology of electrospinning experiments was investigated by using a Field Emission-Scanning Electron Microscope (FE-SEM), Zeiss (Auriga). The diameters of 20 fibers were randomly measured using Digimizer 4.1 software.

Design and analysis of experiments

The Taguchi method was introduced to reduce the period and cost of product development. In the Taguchi method, it is possible to control the alternations made by uncontrollable parameters, which are not considered in the classical DoE design. It works by converting the amount of target features to a signal-to-noise (S/N) ratio for measuring the performance of the level of controlling parameters in contradiction to these parameters. The S/N ratio is the favorite signal ratio for the non-favorite random noise and displays the quality of the experimental values. Three dissimilar functions were utilized as the following target based on the S/N ratio: "larger is better", "nominal is best" and "smaller is better". In addition, analysis of variance (ANOVA) was utilized to conclude the statistical significance of the electrospinning factors. By using the ANOVA and S/N ratios, the optimum condition of electrospinning can be achieved. Finally, the confirmation test of experiments was performed utilizing the optimum electrospinning conditions, which were determined by the Taguchi optimization method and, by this means, validation of the optimization was tested. In the current research, electrospinning factors were optimized for the diameter of the fibers that occurred in the electrospinning of the PMMA material. Two different levels of voltage (kV), three levels with altering feed rate (ml/h), tip-to-collector distance (cm), needle gauge and polymer solution concentration were selected as the electrospinning variables. The electrospinning factor levels were selected through the experimental runs to have the proper electrospinning condition and to ensure that fibers rather than particles were created. The L_{18} orthogonal array of the Taguchi method utilized a mixed mode 2**1 × 3**4 in the experimental design. All possible run variables and their levels are given in Table 1 and labeled in Table 2.

Table 1. Five factors and their levels selected in the L_{18} design of experiments array

Variables		Level 1	Level 2	Level 3
A	Voltage (kV)	15	20	
B	Feed rate (ml/h)	1	2	4
C	Tip-to-collector distance (cm)	10	15	20
D	Needle gauges	19	23	27
E	Polymer solution concentration (wt%)	15	20	25

Also, optimization of the electrospinning factors has been done accurately. The performance characteristic function that the smaller is better was utilized for obtaining the optimal electrospinning factors for the diameter of the fibers. The S/N ratio η formulate is expressed as

$$S/N(\eta) = -10 \cdot \log\left(\frac{1}{n}\sum_{i=1}^{n} Y_i^2\right) \tag{1}$$

where Y_i is the achieved value in the experimental test and n is the number of tests. Equation (1) was used to calculate the S/N ratios of five factors and their levels for the fiber diameters. The significance level of the variables for the fiber diameter was determined using the 95% confidence level of the ANOVA. Software Minitab 14 was utilized to optimize the electrospinning process according to the Taguchi approach. Minitab is strong software that is acknowledged to accurately solve numerous statistical issues and improve quality in the areas of engineering, statistics and mathematics.

Results and discussion

Surface morphology and distribution of fiber diameter

The FE-SEM micrographs of the composite fiber morphology in the DoE study and the corresponding average fiber diameters determined are illustrated in Figure 1 and Table 2. Thus, hereby, the discussion of the results is both quantitative and qualitative; the coverage of the qualitative justifications for fiber

Table 2. Experimental results of electrospun polymethyl methacrylate fibers diameter and signal-to-noise (S/N) ratios based on "smaller is better"

Sample no.	Designation	(A) Voltage (kV)	(B) Feed (ml/h)	(C) Distance (cm)	(D) Needle (gage)	(E) Concentration (wt%)	Fiber diameter (±std.dev) (nm)	S/N ratios (dB)
ES#1	$A_1B_1C_1D_1E_1$	1	1	1	1	1	250.30 (±73)	−48.1487
ES#2	$A_1B_1C_2D_2E_2$	1	1	2	2	2	476.40 (±223)	−54.0846
ES#3	$A_1B_1C_3D_3E_3$	1	1	3	3	3	1287.20 (±344)	−62.4781
ES#4	$A_1B_2C_1D_1E_2$	1	2	1	1	2	550.35 (±264)	−55.6767
ES#5	$A_1B_2C_2D_2E_3$	1	2	2	2	3	1129.50 (±318)	−61.3736
ES#6	$A_1B_2C_3D_3E_1$	1	2	3	3	1	329.50 (±186)	−50.5213
ES#7	$A_1B_3C_1D_2E_1$	1	3	1	2	1	386.85 (±203)	−52.8963
ES#8	$A_1B_3C_2D_3E_2$	1	3	2	3	2	462.20 (±113)	−53.5362
ES#9	$A_1B_3C_3D_1E_3$	1	3	3	1	3	993.95 (±448)	−60.7169
ES#10	$A_2B_1C_1D_3E_3$	2	1	1	3	3	1297.85 (±384)	−62.6125
ES#11	$A_2B_1C_2D_1E_1$	2	1	2	1	1	228.10 (±76)	−47.2528
ES#12	$A_2B_1C_3D_2E_2$	2	1	3	2	2	506.90 (±130)	−54.3632
ES#13	$A_2B_2C_1D_2E_3$	2	2	1	2	3	1030.55 (±227)	−60.4576
ES#14	$A_2B_2C_2D_3E_1$	2	2	2	3	1	260.60 (±86)	−48.6662
ES#15	$A_2B_2C_3D_1E_2$	2	2	3	1	2	632.85 (±133)	−56.2051
ES#16	$A_2B_3C_1D_3E_2$	2	3	1	3	2	449.25 (±93)	−53.2237
ES#17	$A_2B_3C_2D_1E_3$	2	3	2	1	3	1686.50 (±455)	−64.8313
ES#18	$A_2B_3C_3D_2E_1$	2	3	3	2	1	292.55 (±94)	−49.5572

morphology includes uniformity, bead formation and fiber diameters and, then, quantitative justifications are established on fiber diameter, S/N ratio and *p*-value. On a global scale, a random fiber distribution is evident in most mat samples due to using a stand-alone mesh collector with little fiber alignment control. Electrospinning polymer solutions involve evaporation of the solvent when the jet is accelerating to the collector; the surface area of the jet increases significantly in a couple of milliseconds and some thermodynamically driven actions can be concluded.

However, some large fibers with a diameter over 1 µm appear to be arranged in ES#3, ES#5, ES#10, ES#13 and ES#17 experiments (Figure 1), comprising of S/N ratios of −62.4781, −61.3736, −62.6125, −60.4576 and −64.8313, respectively. This denotes that approximately less than −60 S/N ratio fiber diameters will likely be over 1 µm (Table 2). This is due to the high concentration of PMMA (wt% = 25) in the DMF solvent; it should be noted that the solution viscosity is proportional to the polymer concentration. Consequently, higher polymer concentration will lead to larger fiber diameter; the significance of this is represented in Table 3, showing a 0.000 *p*-value, which displays basically the highest prominence as final response. Based on the power law relationship, Deitzel et al.[6] concluded that the size of fiber diameter increases by intensifying the polymer concentration. It is acknowledged that applied electrical voltage is one of the factors that influences the fiber diameter; overall, more polymer solution ejected by increasing the voltage causes an increase in the fiber size,[22] as illustrated in ES#10, ES#13 and ES#17 with average diameters of 1297 (±384), 1030 (±227) and 1686 (±455) nm, respectively. Common non-uniform fiber morphologies are found mostly in ES#2, ES#11 and ES#18 with an average diameter variation of 228 (±76)–476 (±223) nm (Figure 1), which could be due to a combination of the low polymer concentration and feed rate. It can be seen that by increasing the combination of the low polymer concentration and feed rate the structure of the fibers is much more uniform.

In addition, large entangled fiber aggregates are shown in most of the experiments, resulting from the hindrance of the fiber structures from the solution jet. This typical phenomenon could be due to the combined effect of the higher feed rate and, consequently, more solution droplets being ejected from the needle tip per hour that do not have sufficient time to be elongated to individual fibers with relatively small fiber sizes received directly from the mesh collector. As a result, fiber aggregates or bundles become more evident due to the lack of fiber stretching/elongation.[5,6,19] On the other hand, short fiber collections are noticed in ES#2, ES#8, ES#11 and ES#17 in the similarity of tip-to-distance value, equal to 15 cm. These shortened

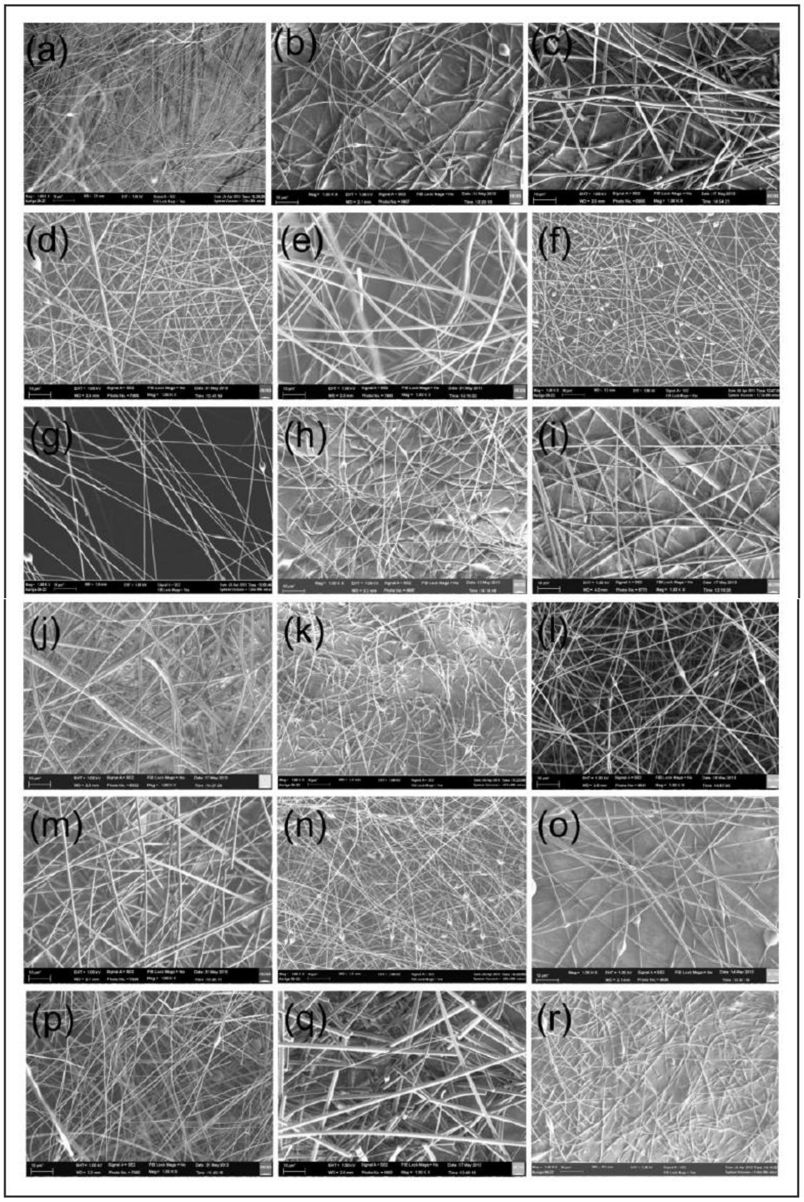

Figure 1. Field emission scanning electron microscope images of electrospun polymethyl methacrylate fibers used in the design of experiments study: (a) ES#1; (b) ES#2; (c) ES#3; (d) ES#4; (e) ES#5; (f) ES#6; (g) ES#7; (h) ES#8; (i) ES#9; (j) ES#10; (k) ES#11; (l) ES#12; (m) ES#13; (n) ES#14; (o) ES#15; (p) ES#16; (q) ES#17; (r) ES#18 (magnification is 1000× and scale bar is 10 μm).

Table 3. Analysis of variance for signal-to-noise ratios of electrospun polymethyl methacrylate fiber diameter

Source	DF	Seq SS	Adj MS	F	P	PCR (%)
A	1	14959	14959	0.39	0.551	0.45
B	2	9861	4930	0.13	0.882	0.29
C	2	6864	3432	0.09	0.916	0.2
D	2	22475	11237	0.29	0.755	0.68
E	2	2939243	1469621	38.13	0.000	89.02
Residual error	8	308352	38544			9.33
Total	17	3301754				100

DF: degree of freedom; SS: sum of squares; MS: mean of squares; PCR: percentage contribution ratio.

fibers can occur as the result of jet whipping instability during electrospinning, which leads to bending and stretching of the jet.[23]

The small-bead defects are seen in ES#1, ES#2, ES#4, ES#7, ES#12 and ES#15 (Figure 1), which may arise from the clogging problem of the middle-concentration (wt% = 20) of PMMA at the needle tip, except in ES#7. Therefore, droplets were formed with the flow instability deteriorating the elongated fiber structures. The number of beads is found to be more in ES#6, ES#8, ES#11, ES#14 and ES#18 as compared to other experiments. The results of the mentioned tests illustrate that production and morphology of fibers are highly associated with solution viscosity.[6,19] It has been reported that when the polymer concentration is low, the number of beads or microspheres created in electrospun fibers can change to electrospraying when the concentration decreases significantly.[19,24,25]

In contrast, the electrospun PMMA fibers become bead-free, as evidenced in ES#3, ES#5, ES#9, ES#10, ES#13, ES#16 and ES#17 (Figure 1). As a result of the high viscosity of the solution (high polymer concentration), bead-free uniform nanofibers were created while 25 wt% polymer concentration was appropriate for PMMA. This may reveal that the creation of the beads is mostly as a result of surface tension, which reduces the surface area. It has been demonstrated that the jet tends to break down into drops without surface tension and that beads are likely to form in low surface tension; also, it can even be justified that the significance of the *p*-value for concentration is prominent for controlling bead formation too. Therefore, fewer beads are created by increasing the polymer concentration and the surface tension. Based on the summarized average fiber diameter data ($d_{average}$ < 300 nm), the minimum average diameter of 228.10 (±76) nm is found in ES#11, followed by ES#1, ES#14 and ES#18 in the average diameter range of 200–300 nm (Table 2). These average values of fiber diameter are the lowest fiber diameters that have been achieved for electrospun PMMA nanofibers in comparison to previous works.

In order to portray a clear view of the subject, histogram plots showing the percentage contribution against the electrospun PMMA fiber diameter range achieved by experimental tests are demonstrated in Figure 2. Upon analyzing the plots it was obvious that ES#11 is the only case study with a high percentage of frequencies distributed in the diameter range of 100–300 nm. Moreover, ES#1, ES#6, ES#14 and ES#18 show a contribution in the range of less than 500 nm. The contribution that was observed in the ES#8, ES#12, ES#15 and ES#16 experiments was in the range of less than 1 µm, along with the previously mentioned experiments. In contrast, ES#2, ES#3, ES#4, ES#5, ES#7, ES#9, ES#10, ES#13 and ES#17 have been shown as being able to fabricate fibers with a diameter higher than 1 µm, taking into consideration that ES#2, ES#4 and ES#7 only had contribution in the more than 1 µm range. It should be noted that ES#5, ES#9, ES#10, ES#13 and ES#17 contributions were distributed over all ranges from less than 1 µm to higher. Overall, ES#17 presented the worst set-up contributions in the range of fiber diameters less than 1 µm, with other contributions mostly allocated to higher than 1.5 µm.

Analyzing and evaluating the results of the experiments using the Taguchi method

Experimental results and signal-to-noise ratios. When all the experiments were carried out based on the L_{18} orthogonal array, the average fiber diameter that occurred during the electrospinning process of the PMMA material was measured. Furthermore, in order to control the fiber diameter, the voltage, feed rate, tip-to-distance, needle gauge and polymer concentration were considered in the development of the mathematical models. It should also be noted that the S/N ratio is the most important deciding factor in the Taguchi method to analyze the experimental data. In this study, the S/N ratio should be the maximum value to get the optimal electrospinning condition in agreement with the Taguchi method. Table 2 shows the experimental results and S/N ratios, which are calculated based on Taguchi's "smaller is better" quality characteristic.

Table 2 shows the S/N ratios of the fiber diameter data achieved from the experimental test results that were calculated according to Equation (1), which will be utilized for establishing the optimum levels of each factor.

Analysis of variance. Table 3 shows the results of the ANOVA that was carried out to conclude the

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